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Neutron Study of Crystal-field Transitions in $ErPO_4$

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Abstract

The crystal-field splitting of the Er^{3+} ground multiplet, $^4I_{15/2}$, in $ErPO_4$ is investigated by inelastic neutron scattering. Four excitations from the Γ_7 ground state to the excited states and several transitions between the excited states have been identified. The observed transition energies and intensities are used to refine the parameters of the crystal-field potential. The calculated magnetic susceptibility, $\chi(T)$, agrees well with experimental values from single-crystal measurements. A comparison of the neutron data with optical absorption and both nonresonance and resonance Raman scattering measurements has been made.

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Introduction

The physical properties of Rare-earth orthophosphates, RPO_4 (R = Tb-Yb), have been the subject of numerous experimental and theoretical studies. These compounds crystallize in the tetragonal zircon structure (space group $I4_1/amd$) in which two equivalent rare-earth ions in a unit cell occupy sites of D_{2d} point-group symmetry. Within the framework of a single-ion approximation, the 4f-states are split by the crystal field according to the local site-symmetry of the rare-earth ions. In general, a crystal-field (CF) model can be applied to interpret the magnetic behavior in which single-ion effects dominate cooperative interactions involving the rare-earth ions. For example, the temperature dependence of the bulk paramagnetic susceptibility of RPO_4 compounds can be well accounted for by CF calculations. Even in the presence of strong coupling of the 4f-states with other collective excitations, (e. g., the effects manifested by a softening of the Young modulus and elastic constants of $TbPO_4$ and $TmPO_4$ at low temperatures[1,2] and by the mixing of CF and phonon excitations in the Raman spectra[3] of $YbPO_4$) the CF concept is still useful as a basis for further theoretical studies.[4,5]. We have recently initiated a systematic study of the CF excitations in the stoichiometric RPO_4 compounds using inelastic neutron scattering. Here we report the results of measurements and analysis of the Er^{3+} CF states in the pure compound $ErPO_4$.

Experimental Details

About 100 g of polycrystalline powder of $ErPO_4$ was prepared by the technique of precipitation from molten urea.[6] The powder was then pressed into pellets and annealed at 1200°C in air for 24 hrs to improve the crystalline quality. The sample was examined by x-ray and neutron powder diffraction and was found to have the appropriate zircon structure. An R-factor of 5.3% was obtained in a Rietvelt analysis of the neutron powder data. No impurity phases were observed within the experimental uncertainty.

The inelastic neutron-scattering (INS) experiments were performed using the HRMECS chopper spectrometer at the Argonne spallation neutron source IPNS. Experimental procedures were the same as those described previously in a CF study of $TmPO_4$.[7] The energy resolution (full-width-at-half-maximum) of the HRMECS spectrometer varies with energy transfer but is approximately 2-4% of the incident neutron energy (E_0) over the neutron energy-loss spectrum. To fully explore the CF and phonon excitations up to 150 meV, four incident energies, 20, 40, 80 and 200 meV were chosen for the studies at 15 K. The 20 meV run was repeated at 30, 100 and 296 K in order to study the temperature dependence of the CF transitions in the 0 - 15 meV region. The magnetic origin of the CF peaks was identified by an examination of the temperature and momentum-transfer dependence of the observed intensities and by comparison with the spectra of the nonmagnetic, isostructural compound $LuPO_4$. The data were corrected for background scattering by subtracting the empty container runs. Measurements of the elastic incoherent scattering from a vanadium standard provided detector calibration and intensity normalization.

Results and Discussion

The Er^{3+} $^4I_{15/2}$ ground multiplet of $ErPO_4$ is split by the tetragonal crystal field into 4 Γ_6 and 4 Γ_7 Kramers doublets. Excitations (or de-excitations) between any two doublet states and elastic scattering within a doublet are allowed by the selection rules for magnetic dipole transitions in a neutron scattering experiment. Transitions to the next multiplet, $^4I_{13/2}$, which is located at energies over 800 meV were not observable in the present neutron experiment. Fig. 1 shows the observed neutron spectra obtained with incident energies of 20, 40 and 80 meV. Sharp CF peaks labeled in the order of B to G, and weak, unresolved CF features H to K were observed at low temperatures. The peak A at zero energy consists of nuclear elastic scattering and CF transitions within the doubly degenerate doublet states. Peaks B', C' and B, C represent

the de-excitation (neutron energy-gain) and the excitation (neutron energy-loss) processes, respectively, of the same CF transitions. The peaks D, E, F and G originate from thermally occupied excited states, as indicated by the temperature dependence of their intensities. The observed position of a CF peak is equal to the energy separation of the two CF states, $\langle i|$ and $\langle j|$, that participate in the transition, and the intensity is proportional to the square of the matrix element $\langle i|J_\perp|j\rangle$ (where $J_\perp$ is the component of the total angular-momentum operator perpendicular to the neutron wave-vector). If the CF-state energies and wavefunctions are obtained from a diagonalization of a Hamiltonian which contains a parameter set for the CF potential, the neutron scattering function, S(E), can be calculated in a straightforward manner as described elsewhere[7]. In practice, the CF parameters for the system under study are not known, and the goal is to find a set of CF parameters which produces calculated spectra that are consistent with the observed CF peak energies and intensities at all temperatures.

The CF model employed here is the same as that used previously by other workers[10] for RPO_4, namely, a single-ion model based on the scheme of intermediate-coupling using the spherical-tensor formalism. The Hamiltonian, associated parameters, and underlying assumptions of the theory have been treated in great detail elsewhere[9,10]. The diagonalization of the total Hamiltonian was executed by a computer code written by the Crosswhites[10]. The lowest 96 free-ion Russell-Saunders states were used to calculate the required matrix elements. The parameters for the free-ion part of the Hamiltonian were taken from those for Er-doped $LuPO_4$ obtained previously from optical spectroscopy by Hayhurst *et al.* [8] and were fixed throughout the calculations.

The Er ion site-symmetry (D_{2d}) in $ErPO_4$ requires the CF part of the Hamiltonian to be characterized by five parameters, B_0^2, B_0^4, B_4^4, B_0^6 and B_4^6. In order to fit the neutron spectra, we first obtained a set of CF parameters for $ErPO_4$ by a scaling of the CF parameters established previously for $TmPO_4$ from an INS study[7]. The scaling of the CF parameters between different

isostructural rare-earth compounds has been described[11] previously in the CF treatments of high-T_c superconductors. We found that the calculated CF level structure using this initial parameter set already closely resembled the pattern of the observed CF excitations. A subsequent fit to the neutron data converged rapidly, yielding calculated energies in good agreement with experimental results for all of the transitions. All of the observed CF peaks and weak features shown in Fig. 1 were accounted for by the calculations. The calculated scattering functions agreed with the observed CF transition energies and intensities at all temperatures. We have also calculated the magnetic susceptibility for $ErPO_4$ according to the Van Vleck formalism[12] using the CF wavefunctions and energies, and find good agreement between the calculated and measured susceptibility for both single-crystal (see Fig. 3) and powder[13] samples.

The crystal-field level scheme for the Er^{3+} $^4I_{15/2}$ ground multiplet determined by the INS study (Fig. 2) agrees with that obtained from optical spectroscopy[14-16] except for two energy levels, i. e., the third Γ_7 state (neutron: 17.1 meV, Raman: 13.0 meV) and the highest Γ_6 state (neutron: 40 meV, Raman: 33.4 meV). The calculated position of the highest Γ_6 state was at 40 meV but excitations to this state were not observed in the INS experiment because of the very small matrix elements. An attempt to assign the third Γ_7 state at 13 meV as was done in the optical data analysis did not yield a good fit to the overall INS data. The excitations from the ground state to the first two levels (the Γ_6 state at 4.08 and the Γ_7 state at 6.60 meV) are by far the most intense features in the INS and in the resonance and nonresonance Raman scattering[14-16] experiments, and they are in very good agreement. The transitions to the third Γ_7 state at 13.0 meV in the Raman spectra were weak and were observed only along the incident and scattered photon polarization parallel to the crystallograhic c-axis. A direct comparison of the observed Raman intensities and polarization patterns with calculations based on the Judd-Ofelt theory has not been satisfactory.[15-17] At present, the reason for the disagreement of these two energy levels between the INS and optical studies is not known. We have accepted the present assignment because the calculated spectra agree well with all the observed neutron data; the CF

parameters are consistent with those for $TmPO_4$ through a scaling of the different rare-earth 4f radial wavefunctions. The calculated magnetic susceptibility, as compared to that using the CF parameters[8] obtained from the optical data of Er-doped $LuPO_4$, is in better agreement with the experimental susceptibility data. Obviously, additional studies of the RPO_4 series are needed in order to clarify the CF level structure of $ErPO_4$, and such investigations are currently in progress at IPNS.

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References

1. R. T. Harley and D. I. Manning, J. Phys. **C 11**, L633 (1978).
2. V. I. Sokolov, Z. A. Kazei, N. P. Kolmakova, and T. V. Solov'yanova, Sov. Phys. JETP **72**, 524 (1991).
3. P. C. Becker, G. M. Williams, N. M. Edelstein, J. A. Koningstein, L. A. Boatner and M. M. Abraham, Phys. Rev. B **45**, 5027 (1992).
4. S. Xia, G. M. Williams and N. M. Edelstein, Chem. Phys. 138, 255 (1989).
5. S. Xia, Int. J. Mod. Phys. B **6**, 59 (1992).
6. M. M. Abraham, L. A. Boatner, T. C. Quinby, D. K. Thomas, and M. Rappaz, Radioactive Waste Management **1**, 181 (1980).
7. C.-K. Loong, L. Soderholm, M. M. Abraham, L. A. Boatner, and N. M. Edelstein, submitted to J. Chem. Phys.
8. T. Hayhurst, G. Shalimoff, N. Edelstein, L. A. Boatner, and M. M. Abraham, J. Chem. Phys. **74**, 5449 (1981).
9. B. G. Wybourne, Spectroscopic Properties of Rare Earths, (John Wiley & Sons, New York) 1965.
10. H. M. Crosswhite and H. Crosswhite, J. Opt. Soc. Am. **B1**, 246 (1984), and W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, J. Chem. Phys. **90**, 3443 (1989).
11. L. Soderholm, C.-K. Loong, G. L. Goodman, and B. D. Dabrowski, Phys. Rev. **B43**, 7923 (1991), and G. L. Goodman, C.-K. Loong, and L. Soderholm, J. Phys.: Condens. Matter **3**, 49 (1991).
12. J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (London: Oxford University Press, 1932).
13. G. Will, W. Lugscheider, W. Zinn, and E. Patscheke, phys. stat. sol. (b) **46**, 597 (1971).
14. P. C. Becker, G. M. Williams, R. E. Russo, N. Edelstein, J. A. Koningstein, L. A. Boatner, and M. M. Abraham, Optics Lett. **11**, 282 (1986).

15. P. C. Becker, N. Edelstein, G. M. Williams, J. J. Bucher, R. E. Russo, J. A. Koningstein, L. A. Boatner and M. M. Abraham, Phys. Rev. **B 31**, 8102 (1985).

16. G. M. Williams, P. C. Becker, N. Edelstein, L. A.Boatner, and M. M. Abraham, Phys. Rev. B **40**, 1288 (1989).

17. P. C. Becker, N. Edelstein, B. R. Judd, R. C. Leavitt and G. M. S. Lister, J. Phys. **C 18**, L1063 (1985).

Figure Captions

Figure 1. The observed scattering functions of $ErPO_4$. Main figure: S (E) obtained with incident energy E_0 = 20 meV at 30 K. Insets: (a) the 5 - 15 meV region with E_0 = 20 meV at 30 K, (b) the 5 - 35 meV region with E_0 = 40 meV at 30 K, and (c) the 10 - 40 meV region with E_0 = 80 meV at 15 K.

Figure 2. A schematic diagram of the splitting of the Er^{3+} $^4I_{15/2}$ ground multiplet by crystal field into 4 Γ_6 + 4 Γ_7 Kramers doublets. The transitions labels refer to the experimentally observed transitions shown in Fig. 1.

Figure 3. The calculated and measured inverse magnetic susceptibility of $ErPO_4$ with the applied magnetic field perpendicular and parallel to the crystallographic c-axis.

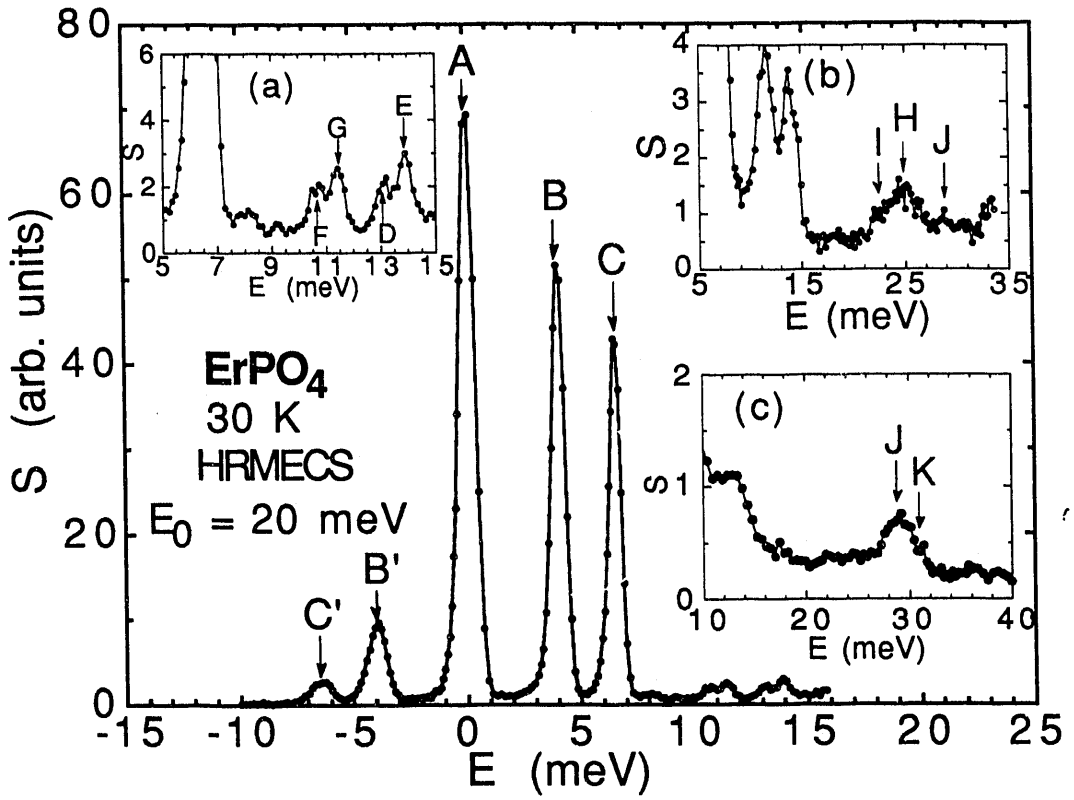
S (arb. units)
E (meV)
ErPO4
30 K
HRMECS
E0 = 20 meV
A
B
C
B'
C'
(a)
G
E
F
D
(b)
H
I
J
(c)
J
K

Fig. 1

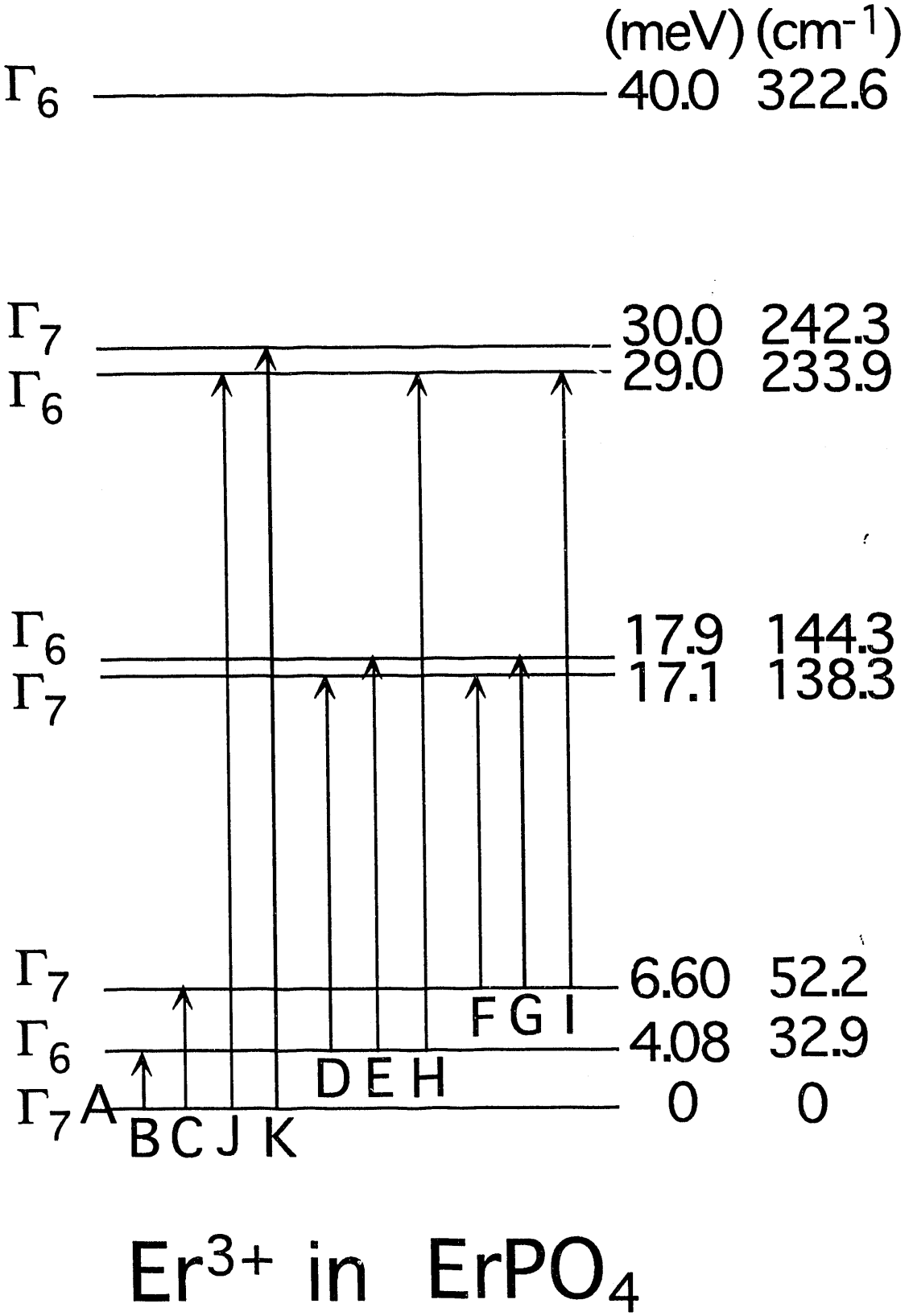
(meV) (cm-1)
Γ6
40.0 322.6
Γ7
30.0 242.3
Γ6
29.0 233.9
Γ6
17.9 144.3
Γ7
17.1 138.3
Γ7
6.60 52.2
Γ6
4.08 32.9
Γ7
0 0
A
B C J K
D E H
F G I
Er3+ in ErPO4

Fig. 2

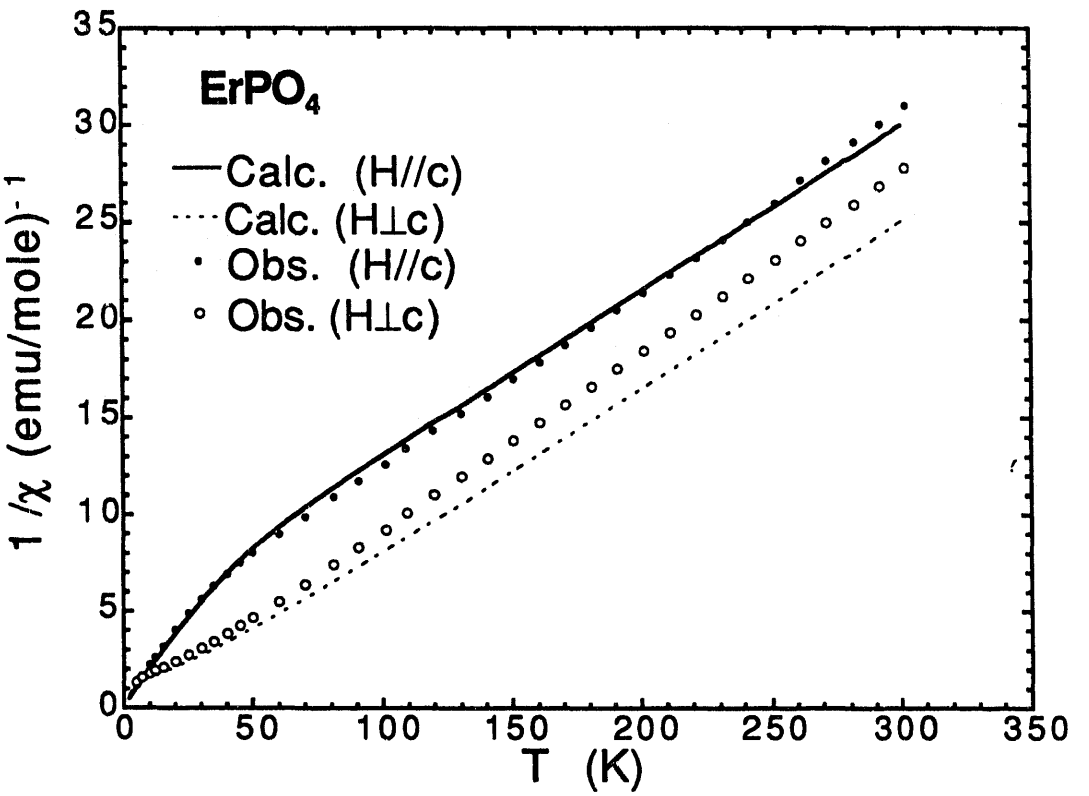
ErPO4
Calc. (H//c)
Calc. (H⊥c)
Obs. (H//c)
Obs. (H⊥c)
1 /χ (emu/mole)-1
T (K)
0
5
10
15
20
25
30
35
0
50
100
150
200
250
300
350

Fig. 3

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